



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09J 167/00, 177/12	A1	(11) International Publication Number: WO 95/18191 (43) International Publication Date: 6 July 1995 (06.07.95)
(21) International Application Number: PCT/US94/14782 (22) International Filing Date: 23 December 1994 (23.12.94) (30) Priority Data: 175,330 29 December 1993 (29.12.93) US 283,011 29 July 1994 (29.07.94) US (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US). (72) Inventors: MILLER, Richard, Anthony; 304 Coralwood Drive, Kingsport, TN 37663 (US). GEORGE, Scott, Ellery; 4005 Foxfire Lane, Kingsport, TN 37664 (US). BARRETT, Alicia, Elaine; 3318 Oak Village Drive, Tyler, TX 75707 (US). PARSONS, Theron, Edward, III; 1245 Watauga Street, Kingsport, TN 37660 (US). MONTGOMERY, Mark, Anthon; 3925 Cambridge Circle, Kingsport, TN 37660 (US). (74) Agent: MONTGOMERY, Mark, A.; P.O. Box 511, Kingsport, TN 37662-5075 (US).		(81) Designated States: AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: WATER-DISPERSIBLE ADHESIVE COMPOSITION AND PROCESS		
(57) Abstract Disclosed is a water-dissipatable or dispersible adhesive composition that is useful in forming paper articles and other products that can be recycled through repulping in both neutral and alkaline media. The water-dispersible adhesive composition is preferably a hot melt adhesive that is a low molecular weight, branched copolyester containing a sulfomonomer. Additional utility for the invention resides in the manufacture of recyclable articles where insolubility in body fluids combined with solubility in tap water are required.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

WATER-DISPERSIBLE ADHESIVE COMPOSITION AND PROCESS

Field of the Invention

5 The present invention is directed to a water-
dispersible adhesive composition. More particularly,
the present invention is directed to a hot melt adhesive
composition that, due to its water-dispersibility, is
repulpable, allowing paper products, nonwoven
10 assemblies, and other disposable products to be more
effectively recycled. The present invention is also
directed to a hot melt adhesive composition containing
polyester that is water dispersible while maintaining
excellent adhesive properties.

15 Background of the Invention

Many adhesives including hot melt adhesives are
useful for bonding various substrates together such as
wood, paper, plastics, and textiles, as well as other
materials. One use for which hot melt adhesives are
20 well suited is the fabrication of corrugated paper
board. Hot melt adhesives, useful for producing
corrugated paper board, must have high bond strength
under conditions of shock, stress, high humidity, and
extremes of temperature encountered in transportation
25 and storage. In addition, the melt point, wetting time,
initial tack, setting time, pot life, and general
handling qualities on automatic corrugated board
machinery are essential considerations.

At present, it is very desirable to recycle paper,
30 paper products, and other disposable products to
conserve material resources and to avoid large additions
to landfill space. It is thus a general practice in the
paper industry to recover the used and waste corrugated
material and repulp the material for use in the

preparation of other materials such as cardboard. The use of polyolefin hot melt adhesives to close or seal cartons made from corrugated material has presented problems in regard to repulpability of the used boxes or

5 cartons (see U.S. Patents 4,070,316; 4,127,619; 4,146,521; 4,460,728; 4,471,086; and 4,886,853). In fact, all the presently available hot melt and pressure sensitive adhesives are largely water insoluble and very difficult to disperse during the repulping process.

10 This fact makes certain paper products, in which adhesives are necessarily utilized, unattractive since failure to disperse the insoluble adhesives results in lower quality recycled paper having variable composition and nonuniformity and thus, lower product value.

15 One approach to avoid the presence of insoluble adhesives in the recycled paper products is to use adhesives whose density is different from the density of water and pulp in water, thus permitting gravitational separation. However, this requires separation steps

20 which can increase the recycling costs of the paper products containing adhesives.

Another approach could be to use a water soluble adhesive that would be separated from the pulp and dispersed into the water during repulping. This type of

25 adhesive would remain in the water when the pulp is recovered. However, presently available water soluble or dispersible adhesives are "natural" adhesives such as dextrans, cellulose gums, and animal glues derived from the hides and bones of animals and these adhesives have

30 lower strength, fail to adhere well to paper and wood stocks with coatings or heavy ink applications, and sometimes require special treatment and handling because of their high viscosity. Therefore, the use of these adhesives, while being easily recyclable, is quite low

due to poor adhesive characteristics. Attempts to produce synthetic water-dispersible hot melt adhesive compositions have heretofore been unsuccessful due to resulting poor adhesive properties such as thermal stability, low strength, poor viscosities and low cold flow resistance. Additionally, costs and ease in manufacturing have precluded their use (see U.S. Patents 3,919,176 and 5,098,962).

In addition to paper and paper products, there are many disposable products, such as diapers, in which hot melt adhesives are used. The use of current hot melt adhesives in these products complicate attempts to recycle products and separate out the insoluble sticky hot melt adhesives.

In light of the above, it would be very desirable to produce a water-dispersible adhesive, particularly a hot melt adhesive, at reasonable costs that maintains the desirable properties of presently available adhesives.

Summary of the Invention

The water-dispersible adhesive composition according to the present invention comprises a branched water-dispersible polyester composition made of the residues or moieties of reaction products;

- (I) at least one difunctional dicarboxylic acid which is not a sulfomonomer;
- (II) 2 to 15 mol percent, based on the total of all acid, hydroxyl and amino equivalence, of residues of at least one difunctional sulfomonomer containing at least one sulfonate group bonded to an aromatic ring wherein the

functional groups are hydroxyl,
carboxyl, or amino;

(III) at least one diol or a mixture of a
diol and a diamine comprising:

5

(A) 0.1 to 85 mol percent, based on
the total mol percent of diol
moieties or diol and diamine
moieties, of a diol or diamine
having the formula $H(-OCH_2CH_2-)_nOH$
and $HRN(\uparrow OH_2CH_2O\uparrow)_nNHR$ wherein n
10 is 2 to 20 and R is hydrogen or
 C_1-C_6 alkyl provided that the mol
percent of such moieties is
inversely proportional to the
value of n ;

15

(B) 0.1 to 15 mol percent, based on
the total mol percent of diol
moieties or diol and diamine
moieties, of moieties of a poly-
20 (ethylene glycol) having the
formula $H(-OCH_2CH_2-)_nOH$ wherein n
is 2 to 500, provided that the mol
percent of such moieties is
inversely proportional to the
value of n ; and

25

(C) 0 to greater than 99 mol percent
of the diol component or diol and
diamine mixture being selected
from the group consisting of a
glycol and a mixture of glycol and
30 diamine having two $-NRH$ groups,
the glycol containing two
 $-C(R^1)_2-OH$ groups wherein R^1 in
the reactant is a hydrogen atom,

30

an alkyl of 1 to 5 carbon atoms,
or an aryl group of 6 to 10 carbon
atoms;

- 5 (IV) 0 to 40 mol % of a difunctional monomer
reactant selected from the group
consisting of hydroxycarboxylic acids
having one $-C(R-)_2-OH$ group, amino-
carboxylic acids having one $-NRH$ group,
10 aminoalkanols having one $-C(R-)_2OH$
group and one $-NRH$ group and mixtures of
said difunctional reactants wherein R
in the reactant is hydrogen or an alkyl
group of 1 to 6 carbon atoms; and
- 15 (V) 0.1 to 40 mol % of a "multifunctional"
or "branch-inducing" reactant
containing at least three functional
groups selected from hydroxyl,
carboxyl, amino, and mixtures thereof;
- 20 the polymer containing substantially equal mol
proportions of acid equivalents (100 mol %) and
diol or diol and diamine equivalents (100 mol %)
wherein at least 20 weight percent of the groups
linking the moieties of the monomeric units are
ester linkages and wherein the inherent viscosity
25 is at least 0.1 dL/g measured in a 60/40 parts by
weight solution of phenol/tetrachloroethane at 25°C
and at a concentration of 0.25 g of polymer in 100
ml of the solvent, the glass transition temperature
 T_g is no greater than 20°C, and the ring and ball
30 softening point is at least 70°C.

Alternatively, the water-dispersible adhesive
composition according to the present invention can be a
blend of two different polyesters that comprises:

- (1) 20 to 80 weight percent of the linear water-dispersible polyester composition made of the residues or moieties of reaction products;
- 5 (i) at least one difunctional dicarboxylic acid which is not a sulfomonomer;
- (ii) 4 to 25 mol percent, based on the total of all acid, hydroxyl and amino equivalence, of residues of at least one difunctional sulfomonomer containing at
- 10 least one sulfonate group bonded to an aromatic ring wherein the functional groups are hydroxyl, carboxyl, or amino;
- (iii) at least one diol or a mixture of a diol and a diamine comprising:
- 15 (A) at least 15 mol percent, based on the total mol percent of diol moieties or diol and diamine moieties, of a diol or diamine having the formula $H(-OCH_2CH_2-)_nOH$ and $HRN-(OH_2CH_2O)_nNHR$ wherein n is 2
- 20 to 20 and R is hydrogen or C_1-C_6 alkyl,
- (B) 0.1 to less than 15 mol percent, based on the total mol percent of diol moieties or diol and diamine moieties, of moieties of a poly-
- 25 (ethylene glycol) having the formula $H(-OCH_2CH_2-)_nOH$ wherein n is 2 to 500, provided that the mol percent of such moieties is inversely
- 30 proportional to the value of n; and,
- (iv) 0 to 40 mol percent moieties of a difunctional monomer reactant selected from hydroxycarboxylic acids, amino-

- 5 carboxylic acids and aminoalkanols; the
polymer containing substantially equal
mol proportions of acid equivalents (100
mol %) and diol or diol and diamine
equivalents (100 mol %) wherein at least
20 weight percent of the groups linking
the moieties of the monomeric units are
ester linkages and wherein the inherent
viscosity is at least 0.1 dL/g measured
10 in a 60/40 parts by weight solution of
phenol/tetrachloroethane at 25°C and at a
concentration of 0.25 g of polymer in 100
ml of the solvent; and
- (2) 20 to 80 weight percent of the branched water-
15 dispersible polyester made of the moieties of
reaction products;
- (a) at least one difunctional dicarboxylic
acid which is not a sulfomonomer;
- (b) one to 20 mol percent, based on the total
20 of acid, hydroxyl and amino equivalents,
of residues of at least one difunctional
sulfomonomer containing at least one
sulfonate group bonded to an aromatic
ring wherein the functional groups are
25 hydroxyl, carboxyl, or amino;
- (c) at least one difunctional reactant
selected from a glycol or a mixture of
glycol and diamine having two -NRH
groups, the glycol containing two
30 -C(R¹)₂-OH groups wherein R in the
reactant is hydrogen or an alkyl group of
1 to 6 carbon atoms, and R¹ in the
reactant is a hydrogen atom, an alkyl of

1 to 5 carbon atoms, or an aryl group of 6 to 10 carbon atoms;

5 (d) 0 to 40 mol % of a difunctional reactant selected from hydroxycarboxylic acids having one $-C(R)_2-OH$ group, amino-carboxylic acids having one $-NRH$ group, amino-alcohols having one $-C(R)_2-OH$ group and one $-NRH$ group, or mixtures of said difunctional reactants wherein R in
10 the reactant is hydrogen or an alkyl group of 1 to 6 carbon atoms; and

(e) 1 to 40 mol % of a "multifunctional" or "branch-inducing" reactant containing at
15 least three functional groups selected from hydroxyl, carboxyl, amino, and mixtures thereof;

wherein all stated mol percents are based on the total of all acid, hydroxyl, and amino group containing reactants being equal to 200 mol
20 percent, and wherein the polymer containing a portion of the acid-group containing reactants (100 mol percent acid) to hydroxyl and amino-group containing reactants (100 mol %).

The present invention also further comprises a
25 process of applying the above water-dispersible adhesive composition between two substrates to form a laminate. The adhesive can later be separated from the substrates in recycling by repulping the entire laminate structure. This invention comprises applying the above water-
30 dispersible adhesive composition in liquid form to a surface of a substrate and, while remaining in the liquid form, applying a second surface of a substrate to the water-dispersible adhesive composition thereby forming an article of manufacture that comprises the

water-dispersible adhesive composition laminated between two substrates or two surfaces of a substrate.

The present invention also comprises the bonded articles of manufacture having the adhesive composition between two substrates such as in carton sealings, corrugated board and diaper construction.

Detailed Description of the Invention

The applicants have unexpectedly discovered an improved adhesive composition that can be applied as a liquid dispersion (aqueous or solvent) on substrates as well as by hot melt application. The inventive adhesive composition not only has good aqueous adhesive properties but also has excellent hot melt adhesive properties and is totally recyclable when the products containing the adhesive are recycled by repulping. The present adhesive composition is easily repulpable and removed from the fibers from paper or wood pulp used in disposable products, particularly in the preferred hot melt applications. The adhesive according to the present invention permits recycling of disposable products at significantly reduced processing costs without affecting the physical properties of the adhesive and resulting article.

Certain water-dispersible polyester compositions are described in detail in U.S. Patents 3,734,874; 3,779,993; 4,233,196; and 4,335,220, the disclosures of which are incorporated herein by reference in their entirety.

The water-dispersible adhesive composition according to the present invention that can be a single polyester is a branched water-dispersible polyester made of the residues or moieties of reaction products; (I); (II); (III); (IV) and (V) above.

Alternatively, the water-dispersible adhesive composition according to the present invention is a blend of two different polyesters that comprises: (1) 20 to 80 weight percent of the linear water-dispersible polyester composition made of the residues or moieties of reaction products; (i); (ii); (iii); and (iv) above and (2) 20 to 80 weight percent of the branched water-dispersible polyester made of the moieties of reaction products; (a); (b); (c); (d); and (e) above.

Although the inventive single polyester water-dispersible adhesive composition and the inventive water-dispersible adhesive composition that is a blend of two different polyesters have different amounts of monomers and a different mix of groups of monomers, some specific groups of suitable monomers and preferred monomers of these groups are the same as is illustrated below.

The sulfonate-containing, water-dispersible, adhesives and polyesters of this invention comprise polyesters, including polyesteramides, having repeating, alternating residues or moieties of one or more dicarboxylic acid which is not a sulfomonomer and one or more diols or a combination of one or more diols and one or more diamines wherein the mol percentages are based on 100 mol percent dicarboxylic acid residues and 100 mol percent diol or diol and diamine residues, for a total of 200 mol percent. Alternatively, the polyesters can include residues of monomers having mixed functionality such as hydroxycarboxylic acids, aminocarboxylic acids and/or aminoalkanols.

Examples of suitable difunctional dicarboxylic acid monomers used to make the residue of (I), (i), and (a) include aliphatic dicarboxylic acids, alicyclic dicarboxylic acids, aromatic dicarboxylic acids, or

mixtures of two or more of these acids. Examples of preferred suitable dicarboxylic acids include succinic; glutaric; adipic; azelaic; sebacic; fumaric; maleic; itaconic; 1,4-cyclohexanedicarboxylic; 1,3-cyclohexane-
5 dicarboxylic; phthalic; terephthalic; and isophthalic. If terephthalic acid is used as the dicarboxylic acid component of the polyester, superior results are achieved when at least 5 mol percent of one of the other acids is also used. It should be understood that the
10 use of the corresponding acid anhydrides, esters, and acid chlorides of these acids is included in the term "dicarboxylic acid".

The difunctional sulfo-monomer component of (II), (ii), and (b) is preferably a dicarboxylic acid or ester
15 thereof containing a metal sulfonate group or a glycol containing a metal sulfonate group or a hydroxy acid containing metal sulfonate group. The cation of the sulfonate salt can be NH_4^+ , or the metal ions Li^+ , Na^+ , K^+ , Mg^{++} , Ca^{++} , Cu^{++} , Ni^{++} , Fe^{++} , Fe^{+++} and the like.

20 Residue or reactant (II), (ii), and (b) in the polyester of the present invention is a difunctional monomer containing a $-\text{SO}_3\text{M}$ group attached to an aromatic nucleus, wherein M is hydrogen, NH_4^+ , or a metal ion. The difunctional monomer component may be either a
25 dicarboxylic acid or a diol adduct containing a $-\text{SO}_3\text{M}$ group. The cation of the sulfonate salt group can be NH_4^+ , or the metal ions Li^+ , Na^+ , K^+ , Mg^{++} , Ca^{++} , Cu^{++} , Ni^{++} , Fe^{++} , Fe^{+++} and the like. Preferred are monovalent cations, such as NH_4^+ , Li^+ , Na^+ , and K^+ , when
30 stability in water is desired.

The $-\text{SO}_3\text{M}$ group is attached to an aromatic nucleus, examples of which include benzene, naphthalene, anthracene, diphenyl, oxydiphenyl, sulfonyldiphenyl, and methylenediphenyl.

The cationic portion of a nonmetallic sulfonate group optionally present in reactant (II), (ii), and (b) is a nitrogen-based cation derived from nitrogen-containing bases which may be aliphatic, cycloaliphatic or aromatic basic compounds that have ionization constants in water at 25°C of 10^{-3} to 10^{-10} , preferably 10^{-5} to 10^{-8} . Especially preferred nitrogen-containing bases are ammonia, dimethylethanolamine, diethanolamine, triethanolamine, pyridine, morpholine, and piperidine, due to availability, cost, and usefulness. Such nitrogen-containing bases and cations derived therefrom are described in U.S. Patent No. 4,304,901, the disclosure of which is incorporated herein by reference in its entirety.

It is preferred that reactant (II) be present in a concentration of 4 to 12 mol percent, more preferably 6 to 10 mol percent, with a mol percent of 8 being most preferred based on total acid equivalents. At amounts below 4 mol percent the polyester is less repulpable whereas at amounts above 12 mol percent the polyester is a little too water-sensitive.

It is preferred that reactant (ii) and, independently, reactant (b) be present in an amount of 2 to 25 mol percent, more preferably 4 to 15 mol percent, based on the total acid equivalents.

Examples of preferred diols of (III) (A) and (iii) (A), due to availability, include diethylene glycol, triethylene glycol, and mixtures thereof. The preferred concentration of (III) (A) is 10 to 80 mol percent, however, when these are the preferred diols of (III) (A) the concentration is 20 to 80 mol percent. At amounts outside this range of 20 to 80 the polyesters have lower softening points and higher Tg than what is most desired.

The moieties of (III) (A) and (iii) (A) can be the same as (III) (B) and (iii) (B), respectively, when the value n is low. However, it is preferred that (B) be a different moiety and be a poly(ethylene glycol).

5 Examples of suitable poly(ethylene glycols) of (III) (B) and (iii) (B) include relatively high molecular weight polyethylene glycols, some of which are available commercially under the designation "Carbowax" (trade-
10 glycols) having molecular weights of from 500 to 5000 are especially suitable.

The moieties of (B) are preferably at a concentration of 1 to 5 mol percent, particularly when n is 10 to 30, due to the preferably higher softening
15 points. The remaining portion of the glycol component of (III), (iii), and (c) can consist of aliphatic, alicyclic, and aralkyl glycols. Examples of these glycols include neopentyl glycol; ethylene glycol; propylene glycol; 1,3-propanediol; 2,4-dimethyl-2-ethyl-
20 hexane-1,3-diol; 2,2-dimethyl-1,3-propanediol; 2-ethyl-2-butyl-1,3-propanediol; 2-ethyl-2-isobutyl-1,3-propanediol; 1,3-butanediol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; 2,2,4-trimethyl-1,6-hexanediol; thio-
25 diethanol; 1,2-cyclohexanedimethanol; 1,3-cyclohexanedimethanol; 1,4-cyclohexanedimethanol; 2,2,4,4-tetramethyl-1,3-cyclobutanediol; p-xylylenediol and neopentyl glycol. Copolymers may be prepared from two or more of the above glycols. Preferred glycols, due to
30 availability, cost, and usefulness, include neopentyl glycol, ethylene glycol, 1,3-propane diol, 1,4-butane diol, 1,6-hexane diol and cyclohexane dimethanols.

Advantageous examples of difunctional monomer component of (III) and (c) which are diamines include ethylenediamine; hexamethylenediamine;

2,2,4-trimethylhexamethylenediamine; 4-oxaheptane-1,4-diamine, 4,7-dioxadecane-1,10-diamine; 1,4-cyclohexane-bismethylamine; 1,3-cyclohexanebismethylamine; heptamethylenediamine; dodecamethylenediamine, etc.

5 The amount of the moieties III (C) present in the polyester is preferably a minor amount up to 99 mol percent, more preferably 20 to 80 mol percent with a mol percent of 30 to 70 being more preferred due to the preferred balance between the desired low Tg and the
10 desired high softening point.

 Advantageous difunctional components which are aminoalcohols or aminoalkanols include aromatic, aliphatic, heterocyclic, and other types in regard to component (IV), (iv) and (d). Specific examples include
15 5-aminopentanol-1,4-aminomethylcyclohexanemethanol, 5-amino-2-ethyl-pentanol-1, 2-(4- β -hydroxyethoxyphenyl)-1-aminoethane, 3-amino-2,2-dimethylpropanol, hydroxyethylamine, etc. Generally these aminoalcohols contain from 2 to 20 carbon atoms, one -NRH group and one
20 -CR₂-OH group.

 Advantageous difunctional monomer components which are aminocarboxylic acids include aromatic, aliphatic, heterocyclic, and other types in regard to component (IV), (iv), and (d) and include lactams.
25 Specific examples include 6-aminocaproic acid, its lactam known as caprolactam, omega aminoundecanoic acid, 3-amino-2-dimethylpropionic acid, 4-(β -aminoethyl)-benzoic acid, 2-(β -aminopropoxy)benzoic acid, 4-amino-methylcyclohexanecarboxylic acid, 2-(β -aminopropoxy)-
30 cyclohexanecarboxylic acid, etc. Generally, these compounds contain from 2 to 20 carbon atoms.

These moieties (IV) (iv) and (d) are less preferred, due to cost and performance, but they can be present. The concentration of these moieties is preferably below 20 mol percent, more preferably below 10 mol percent, including zero.

Preferred water dispersible linear polyesters of (1) in the polyester blend contain diacid monomer residues that are 75 to 90 mol percent isophthalic acid residues, and 10 to 25 mol percent 5-sodiosulfoisophthalic acid monomer residues; and diol monomer residues of 45 to 100 mol percent diethylene glycol monomer residues and 0 up to 55 mol percent 1,4-cyclohexanedimethanol.

The more preferred water dispersible linear polyesters of (1) have an inherent viscosity of 0.1 to 0.6, preferably 0.2 to 0.5, and a Tg range of 25 to 88°C, preferably 29 to 55°C.

The branched water dispersible polyester of (2) is made of the moieties of the reaction products (a), (b), (c), (d), and (e) above.

Related branched water-dispersible polyesters of (2) above are disclosed in U.S. Patent 5,218,042, the disclosure of which is incorporated herein by reference in its entirety. U.S. Patent 5,218,042 is directed towards increasing the stability of dispersions in water and thus endcaps the acid groups or forms a diol adduct of a dicarboxylic sulfomonomer to maintain dispersion stability. However, the present inventive compositions are not directed towards maintaining a stable emulsion, simply producing an emulsion by pulping and dissolving the hot-melt adhesive in water until it is separated from the fibers. Therefore, endcapping and forming a diol adduct of the sulfomonomer is not a requirement for the present invention.

The polyester compositions are branched by virtue of the presence of a multifunctional reactant (V) and (e) that contains at least three functional groups selected from hydroxyl, carboxyl, and amino. Examples of preferred multifunctional reactants of (V) and (e) are trimethylpropane (TMP), trimethylolethane (TME), glycerine, pentaerythritol, erythritol, threitol, dipentaerythritol, sorbitol, trimellitic anhydride, pyromellitic dianhydride, and dimethylolpropionic acid with TMP being most preferred, due to availability and effective results.

The amount of this branching agent (V) and (e) is preferably below 20 mol percent, more preferably below 10 mol percent, (including the range for (V) of 0.5 to 10), with a concentration of 1 to 7 or 2 to 6 mol percent being most preferred. At very high amounts of branching agent the polyester is prone to gelation whereas at low amounts, such as below 0.5 and 0.1, the polyester has poorer performance and properties.

The dispersible linear polyester composition of (1) is blended with the branched water-dispersible polyester composition of (2) at temperatures greater than 200°C, preferably 225°C, for at least one hour. In the adhesive blend composition according to the present invention the relative amounts of the two polyesters vary from 20 to 80 weight percent of the polyester of (1) and 20 to 80 weight percent of the polyester of (2). The concentration of these two polyesters in the hot melt adhesive composition according to the present invention is preferably greater than 30 but less than 80 weight percent polyester of (1) and greater than 20 but less than 70 weight percent of the polyester of (2). The concentration of the two polyesters is more preferably 40 to 77 weight percent (1) and 23 to 60 weight percent

of (2), even more preferably 60 to 75 weight percent of (1) and 25 to 40 weight percent of (2) with a concentration of the two polyesters in weight percent of 70 (1) and 30 (2) being most preferred. Higher amounts of the polyester of (1) increase the melting point of the final adhesive composition. At amounts of the polyester of (1) higher than 80 weight percent, the adhesive has too high of a melting point to be practical. Higher amounts of the polyester of (2) decrease the melting point of the final adhesive. At amounts of the polyester of (2) higher than 80 weight percent, sometimes higher than 70, the adhesive has too low of a melting point to be practical.

The polyesters according to the present invention preferably have at least 50 weight percent of the linking groups linking the moieties of the monomeric units being ester linkages, more preferably at least 90 weight percent, with an ester linkage weight percent of 100 being most preferred.

The water-dispersible polyesters described herein have an inherent viscosity of at least 0.1 dL/g, preferably 0.2 to 0.5 dL/g, measured in a 60/40 parts by weight solution of phenol/tetrachloroethane at 25°C and at a concentration of 0.25 g of polymer in 100 ml of solvent.

The final adhesive compositions preferably have a number average molecular weight of 2,000 to 20,000 more preferably 3,000 to 10,000. Although it is desirable to have as high a molecular weight as possible to achieve the maximum physical properties, such as tensile strength and peel strength, the melt viscosity also increase as molecular weight increases. Therefore, at very high molecular weights the melt viscosity is too high for many useful applications.

The preferred Tg of the adhesive composition according to the present invention is below 10°C and more preferably varies from 4 to -20°C, with a Tg of 4 to -13°C being most preferred. The Tg (glass transition temperature) of the adhesive compositions of the present invention are preferably as low as possible. Thus Tgs below 4°C and even below 0°C are preferred. Tgs of greater than 0°C have generally higher ring and ball softening point (RBSP) and heat resistance but are not as flexible. A low Tg means that the adhesive compositions will not be brittle, thus, cartons adhered together with the adhesive compositions of the present invention when impacted, even at extremely cold temperatures will not shatter and thus maintain adhesion. However, extremely low Tgs are not easily obtained or at least not easily obtained without greatly affecting some other property, such as lowering the ring and ball softening point.

The hot melt adhesive composition according to the present invention preferably has a viscosity of 1,500 to 30,000 centipoise (1.5 to 30 Pa·s) at 350°F (177°C), more preferably 3,000 to 15,000 cP (3 to 15 Pa·s) at 350°F (177°C) due to ease in application.

The ring and ball softening point (RBSP) of the adhesive composition of the present invention is preferably at least 80°C, more preferably 80 to 100°C. The high temperatures of RBSP are better since this means at higher storage temperatures delamination will not occur. (High RBSP provides delamination resistance).

The adhesive compositions according to the present invention are particularly useful due to their good combination of properties and are suitable for use as adhesives for many substrates including non woven

assemblies (such as non woven polypropylene), paper products (such as paper and paperboard), and wood pulp and are easily recyclable and repulpable. The hot melt adhesives according to the present invention are

5 recyclable/repulpable and improved over prior art repulpable hot melt adhesive compositions in that the set time, temperature sensitivity, compatibility, stability on storage, shear strength, tensile strength, viscosity, and cold flow resistance are improved.

10 The adhesive composition according to the present invention is applied to one substrate with a second substrate being placed on top of the adhesive forming an article having the adhesive laminated between two substrates.

15 The adhesive composition according to the present invention can be applied in liquid form in solvent or in an aqueous solution at a concentration of 10 to 70 weight percent with the remainder being solvent or water or mixtures thereof. Surfactants and other additives

20 can also be present to aid in the dispersibility of the adhesive composition. When applied as a solution, the adhesive compositions are generally applied by conventional processes, such as extrusion coating, spray coating, roll coating, brush coating, dip coating, etc.

25 The adhesive composition according to the present invention is preferably used as a hot melt adhesive. The hot melt adhesive composition is preferably applied in the melt at a temperature of 150 to 200°C to a surface of a substrate and, while remaining molten and

30 pliable, applying a second surface of a substrate to the water-dispersible hot melt adhesive composition thereby forming an article of manufacture that comprises the water-dispersible hot melt adhesive composition

laminated between two substrates or two surfaces of a substrate.

5 The adhesive compositions of the present invention are preferably not crosslinked since that would impair their water dispersibility and repulpability. However, they could be crosslinked, to a certain extent with diisocyanates to improve strength and heat resistance although this is less preferred.

10 The adhesive composition according to the present invention can also contain standard additives including stabilizers, preferably 0.1 to 0.5 weight percent stabilizers. Suitable stabilizers include the antioxidant type and generally consist of sterically hindered phenols, or sulfur or phosphorous substituted phenols. An especially useful antioxidant is
15 Irganox 1010 (trademark) (from Ciba-Geigy, Hawthorne, NY) which is a pentaerythritol tetrakis-3(3,5-di-tertiarybutyl-4-hydroxyphenyl)propionate.

20 Additional additives can be added to raise and lower Tg and RBSP. These include, for example, elastomers, plasticizers, low molecular weight polyolefins, resins, and tackifiers. Although, elastomers can be added to the polyester composition, the presence of such elastomers may be adverse to
25 certain desired properties of the composition. Therefore, it is preferable that the composition of the present invention contain substantially no elastomer. Additionally, the plasticizers such as DOP, DOTP, phenols, glycols, phthalate esters and the like that can
30 be added, can distract from the heat resistance of the final composition lowering the RBSP.

Other additives such as UV light absorbers, nucleating agents, colorants, pigments, solvents, and

fillers can be present in small amounts as needed and known in the adhesive art.

Tackifiers are added to the polyester composition to prevent cold flow and increase the softening point.

5 Tackifiers are typically selected from at least one of the groups consisting of hydrocarbon resins, synthetic polyterpenes, functional copolymers, and rosin esters. Hydrocarbon resins are disclosed in U. S. Patent No. 3,850,858 and functional copolymers, such as

10 styrene-co-maleic anhydride, are well known in the art. Hydrocarbon resins, prepared according to U.S. Patent 3,701,760, polyterpenes, and rosin esters can be used alone or in combinations. These tackifying resins, which preferably have softening points of at least 100°C

15 and most preferably 120°C, can be used in amounts of 10% to 50% by weight of the adhesive composition, preferably 25% to 40% by weight. Suitable resins and rosin esters are the terpene polymers having a suitable ring and ball softening point such as the polymeric, resinous

20 materials including the dimers as well as higher polymers obtained by polymerization and/or copolymerization of terpene hydrocarbons such as the alicyclic, monocyclic, and bicyclic monoterpenes and their mixtures, including allo-ocimene, carene, isomerized

25 pinene, pinene, dipentene, terpinene, terpinolene, limonene, turpentine, a terpene cut of fraction, and various other terpenes. Commercially available resins of the terpene type include the Zonarez (trademark) terpene B-series and 7000 series from Arizona Chemical.

30 Also included are the rosin esters with acid numbers above 5 such as the Zonatac (trademark) resins from Arizona Chemical. Particularly useful materials are terpene mixtures containing a mixture of sulphate terpene, and at least 20% of at least one other terpene

selected from the group consisting of pinene, limonene, or dipentene.

5 These adhesive compositions can also be modified to increase the RBSP and reduce cold flow by including additives such as precipitated calcium carbonates and silicas such as fumed silica. A suitable fumed silica comes from Cabot Corp. as CABOSIL (trademark).

10 The present copolyester composition can be modified with random or alternating styrenic copolymers useful in the compositions of this invention and may be prepared by any of the several methods available for their synthesis. For example, the copolymers may be obtained by solution copolymerization directly from the
15 respective monomers by the incremental additions of the more reactive monomer as taught by U.S. Patent No. 2,971,939 or by a continuous recycle polymerization process described in U.S. Patent Nos. 2,769,804 and 2,989,517. Suitable commercially available random or
20 alternating copolymers include the "Dylark" (trademark) styrene/maleic anhydride copolymers. Suitable blocked copolymers for example from Shell Chemical, include Kraton (trademark) FG-1901X or Kraton FG-1921X linear styrene ethylene-1-butene styrene blocked copolymers. In formulating adhesives or sealants for use herein, the
25 blocked copolymers should be used of 5-20%, preferably 7-12%.

30 Modified polyolefins suitable for use in the present invention are prepared by reacting a polyolefin with unsaturated polycarboxylic acid, anhydride or esters thereof, such as maleic anhydride. In formulating adhesive or sealants for use herein the modified polyolefins should be used in low amounts from 3-15% preferably 5-9%. These modified polyolefins can enhance heat resistance of the composition.

The adhesive composition of this invention can be prepared using one or more modifiers to the branched copolyester, by blending with the polyester at melt temperatures of 177-200°C and mixing until a homogeneous mixture is obtained. A cowles stirrer provides effective mixing for these preparations.

The following examples are intended to illustrate the present invention but are not intended to limit the reasonable scope thereof.

Examples

In the following examples GEL Permeation Chromatography (GPC) is used for determination of the molecular weight distribution averages: M_w , M_n , M_w/M_n (polydispersity), and M_z .

In the following examples the Peel Adhesion Failure Temperature was determined according to the following procedure to find the 180° peeling tension fail. This is determined by subjecting a specimen to a continuous dead weight loading of 100 grams per inch (2.54 cm) of bond width for 10 minutes at a given temperature.

The adhesive is laminated onto 30 pound (13.6 kg) kraft paper to a thickness of 1 mil (2.54×10^{-3} cm) and a width of 1.5 inches (3.8 cm). Another section of kraft paper is placed on top of the adhesive laminate. The test specimen is heat sealed at 122°C at 25 psi (0.17 kPa) for 0.2 seconds. Three specimens are prepared. The bonded peel specimens must condition overnight in a laboratory at 23°C at 50% humidity before testing. The oven temperature is set at 14°C, the three specimens are placed therein, and a 100 gram weight is attached to each. The specimens are conditioned in the oven for 10 minutes, and the temperature is then raised 4°C at 10 minute intervals. The Peel Adhesion Failure

Temperature is the temperature in degrees C at failure (3 test average).

Example 1 - Preparation and Testing of Branched Polyester

5

10

15

20

25

30

Control: A 1000 mL round bottom flask equipped with a ground-glass head, agitator shaft, nitrogen inlet, and a sidearm was charged with 139.4 grams (0.84 mole) of isophthalic acid, 23.4 grams (0.16 mole) adipic acid, 95.4 grams (0.90 mole) diethylene glycol, 31.2 grams (0.30 mole) neopentyl glycol, 6.7 grams (0.05 mole) trimethylol propane, 10.0 grams (0.01 mole) of poly(ethylene glycol), MW = 1000, and 1.05 mL of a 1.46% (w/v) solution of titanium isopropoxide in n-butanol. The flask was purged with nitrogen and immersed in a Belmont metal bath at 200°C for 90 minutes and 220°C for an additional 90 minutes under a slow nitrogen sweep with sufficient agitation. After elevating the temperature to 280°C a vacuum ≤ 0.5 mm was installed 11 minutes to perform the polycondensation. The vacuum was then displaced with a nitrogen atmosphere and the polymer was allowed to cool after removing the flask from the metal bath. An inherent viscosity of 0.371 dL/g was determined for the recovered polymer according to ASTM D3835-79 and a glass transition temperature of 3°C was obtained from thermal analysis by DSC. The polymer was clear and amorphous. Molecular weights as determined by GPC were: $M_n = 10,400$, $M_w = 32,250$, and $M_z = 104,150$. The properties of this resin are illustrated in Table 1. This sample when placed in tap water, pH approximately equal to 8, was insoluble and would not be suitable for application as a repulpable adhesive.

Example 2 - Preparation of Branched Water-Dispersible Polyester

A 1000 mL round bottom flask equipped with a ground-glass head, agitator shaft, nitrogen inlet, and a sidearm was charged with 192.0 grams (1.15 moles) of isophthalic acid, 35.1 grams (0.24 mole) adipic acid, 31.1 grams (0.105 mole) dimethyl-5-sodiosulfoisophthalate, 143.1 grams (1.35 mole) diethylene glycol, 46.8 grams (0.45 mole) neopentyl glycol, 10.05 grams (0.075 mole) trimethylol propane, 30.0 grams (0.03 mole) of poly(ethylene glycol), MW = 1000, and 1.67 mL of a 1.46% (w/v) solution of titanium isopropoxide in n-butanol. The flask was purged with nitrogen and immersed in a Belmont metal bath at 200°C for 90 minutes and 220°C for an additional 90 minutes under a slow nitrogen sweep with sufficient agitation. After elevating the temperature to 280°C a vacuum ≤ 0.5 mm was installed for 15 minutes to perform the polycondensation. The vacuum was then displaced with a nitrogen atmosphere and the polymer was allowed to cool after removing the flask from the metal bath. An inherent viscosity of 0.258 dL/g was determined for the recovered polymer according to ASTM D3835-79 and a glass transition temperature of 9°C was obtained from thermal analysis by DSC. The clear polymer was stabilized with 0.3 grams of Irganox 1010. Molecular weights as determined by GPC were: $M_n = 6,500$, $M_w = 13,200$, and $M_z = 20,800$. The properties of this resin are illustrated in Table 1.

Example 3 - Preparation of Branched Water-Dispersible Polyester

5 A 1000 mL round bottom flask equipped with a ground-glass head, agitator shaft, nitrogen inlet, and a sidearm was charged with 184.0 grams (0.92 moles) of dimethyl cyclohexanedicarboxylate, 23.7 grams (0.24 mole) dimethyl-5-sodiosulfoisophthalate, 95.4 grams (0.90 mole) diethylene glycol, 31.2 grams (0.30 mole) neopentyl glycol, 6.70 grams (0.05 mole) trimethylol propane, and 1.17 mL of a 1.46% (w/v) solution of titanium isopropoxide in n-butanol. The flask was purged with nitrogen and immersed in a Belmont metal bath at 200°C for 90 minutes and 220°C for an additional 90 minutes under a slow nitrogen sweep with sufficient agitation. After elevating the temperature to 280°C a vacuum ≤ 0.5 mm was installed for 10 minutes to perform the polycondensation. The vacuum was then displaced with a nitrogen atmosphere and the polymer was allowed to cool after removing the flask from the metal bath. 10 An inherent viscosity of 0.210 dL/g was determined for the recovered polymer according to ASTM D3835-79 and a glass transition temperature of -4°C was obtained from thermal analysis by DSC. The polymer was clear and nearly colorless. Molecular weights as determined by GPC were: $M_n = 5,800$, $M_w = 10,400$, and $M_z = 15,500$. 15 The properties of this resin are illustrated in Table 1.

Example 4 - Preparation of Branched Water-Dispersible Polyester

30 A 1000 mL round bottom flask equipped with a ground-glass head, agitator shaft, nitrogen inlet, and a sidearm was charged with 128.0 grams (0.77 mole) of isophthalic acid, 23.4 grams (0.16 mole) adipic acid, 23.7 grams (0.08 mole) dimethyl-5-sodiosulfoiso-

phthalate, 95.4 grams (0.90 mole) diethylene glycol, 31.2 grams (0.30 mole) neopentyl glycol, 6.70 grams (0.05 mole) trimethylol propane, 10.0 grams (0.01 mole) of poly(ethylene glycol), MW = 1000, and 1.09 mL of a
5 1.46% (w/v) solution of titanium isopropoxide in n-butanol. The flask was purged with nitrogen and immersed in a Belmont metal bath at 200°C for 90 minutes and 220°C for an additional 90 minutes under a slow nitrogen sweep with sufficient agitation. After
10 elevating the temperature to 280°C a vacuum ≤ 0.5 mm was installed for 10 minutes to perform the polycondensation. The vacuum was then displaced with a nitrogen atmosphere and the polymer was allowed to cool after removing the flask from the metal bath. An
15 inherent viscosity of 0.226 dL/g was determined for the recovered polymer according to ASTM D3835-79 and a glass transition temperature of 13°C was obtained from thermal analysis by DSC. The clear polymer was stabilized with
20 0.3 grams of Irganox 1010. Molecular weights as determined by GPC were: $M_n = 7,300$, $M_w = 14,000$, and $M_z = 22,600$. The properties of this resin are illustrated in Table 1.

Table 1

PROPERTIES OF ADHESIVE COMPOSITIONS

Example No.	(a) Set Time (sec)	(b) Viscosity @177°C cps (Pa·s)	(c) Tensile Strength (mpa) Elongation%	(d) Peel Adhesion Failure Temperature °C	(e) Tg °C	(f) Ring and Ball Softening Point °C
1	7.0	4,120 (4.12)	—	34	3	70
2	6.1	3,840 (3.84)	.09 >1200%	35	9	82
3	4.2	3,570 (3.57)	.03-.09>1200%	30	-13	82
4	3.6	4,630 (4.63)	1.0, 873% elongation	40	13	90

(a) TAPPI Symposium, Recyclable/Repulpable Hot Melts - A Summary, June 1990, by Michael J. Ambrosini

(b) ASTM D3236 Test Method

(c) ASTM 412 Test Method

(d) Kraft to kraft bond

(e) ASTM D3418

(f) ASTM E-28

Example 5 - Repulpability Test (Neutral)*

Approximately 10 grams of each of the adhesives in Examples 2,3 and 4 were melted, dyed, and coated onto white bond copier paper to a thickness of 1.5 to 3.0
5 mils (0.04 to 0.08 mm) with a wire wound rod. The coated paper was then cut to obtain a piece weighing 12 grams. The weighed coated paper was then torn into 1" by 1" (2.54 cm by 2.54 cm) pieces and placed into approximately 1000 mL of tap water in the bowl of a
10 laboratory blender to obtain a solids to liquid consistency of ~1.2% and soaked from 1 to 4 hours. The coated paper and water were agitated at 500 rpm for 10 minutes, at 1,000 rpm for 10 minutes, and 1,500 rpm for 10 minutes. Following agitation, a portion of the
15 slurry was removed from the bowl and diluted to produce a 0.7% solids mixture. This mixture was stirred for 30 seconds and quickly poured into a Buchner funnel that contains a 100 mesh polyester screen. A vacuum pump was attached for a short interval until the water was
20 evacuated from the funnel and a handsheet was formed. The handsheet and screen were then removed from the funnel and excess water was blotted away with Watman 5 filter paper. The handsheet was then weighted and dried on a warm hot plate. The dried handsheet was then
25 inspected for "stickies" using both transmitted and reflected light.

All three examples were completely dispersible, in that during the hour soak in a room temperature neutral solution all dyed coating samples completely separated
30 from copy paper. During agitation, the solution was foamy and a sweet odor was noticed. No adhesive residue (stickies) were on the hand sheet. Thus, there was complete r pulpability. This test showed that the compositions in Examples 2, 3 and 4 were highly water
35 dispersible and repulpable under neutral conditions.

*Tappi, 1993, Hot Melt Symposium Procedure, Barrett

Example 6 - Repulpability in alkaline solution*

5 An alkaline solution was prepared by adding 6.2 g
of NaOH pellets, 3 g of tetrasodium pyrophosphate (TSPP)
and 0.6 ml of Triton (trademark) x-100 surfactant to 400
ml of H₂O at room temperature. The solution was warmed
on a hot plate to 27°C. When the TSPP had dissolved, it
was diluted to 1000 ml and adjusted to a pH of 9-12 with
10 H₂O or base. The solution was then brought to 85°C and
then 1" x 1" (2.54 x 2.54 cm) pieces of coated paper
from Examples 2, 3 and 4 prepared as in Example 5 were
added as the solution was slowly stirred at the blend
station. When coated paper began to de-fiber, the mixer
15 speed was adjusted to give a gentle rolling of slurry.
Mixing was continued for 15-30 minutes. After
defibering for 15-30 minutes, slurry was diluted to 1000
ml and stirred thoroughly to assure a uniform
suspension. The handsheet was formed as in Example 5.
20 The degree of adhesive repulpability was evaluated as in
Example 5.

All three examples were completely dispersible, in
that dyed coating sample began separating from the copy
paper within 5 minutes of entering the heated (85°C)
25 alkaline solution. During the 30 minute agitation the
coating completely dispersed throughout solution. There
was a pale orange color visible in handsheet; however,
no adhesive residue (stickies) was on hand sheet. Thus,
there was complete repulpability. The results indicate
30 that Examples 2, 3 and 4 are repulpable under alkaline
conditions.

*Tappi, 1993, Hot Melt Symposium Procedure, Barrett

Example 7 - Dispersibility of Adhesive Coated Wood Pulp

Wood pulp (5 grams) taken from a Huggies (trade-
mark) brand diaper from Kimberly Clark, was coated with
1.5 grams of the adhesive from Examples 2, 3 and 4 at
5 350°F (177°C). The adhesive coated wood pulp was placed
in one liter of tap water (pH 7.9) at room temperature
for one hour with hand stirring approximately every 10
minutes. The slurry was poured through a 600 mL Hirsch
funnel pulled under vacuum at 25 psi (0.17 kPa) until
10 water is completely removed out of the funnel. The wood
pulp remained in the funnel without any sign of adhesive
present in the funnel. All of the adhesive passed
through the funnel into the container with the water.

15 Example 8 - Solubility of Examples 2, 3, and 4

A one gram sample of each polyester from Examples
2, 3, and 4 was placed in tap water (pH 8.0), deionized
water (pH 7.2) and two simulated body fluids. The first
simulated body fluid containing 10 gms. sodium chloride,
20 4 gms. ammonium carbonate, 1 gm disodium hydrogen
phosphate, and .25 grams histidine monohydrochloride,
dissolved in 1 liter of deionized water, with a final pH
8.0. The second simulated body fluid containing 10
grams sodium chloride, 1 gram lactic acid, and 1 gram
25 disodium hydrogen phosphate, and .25 gram histidine
monohydrogenchloride, dissolved in 1 liter deionized
water, with a final pH of 3.9.

Test Results

Examples 2, 3, and 4 dissolved in less than one hour
30 immersion in tap water and deionized water and remained
insoluble in simulated body fluid solution after
24 hours immersion.

The following examples 1B through 9B are examples
35 of the adhesive composition according to the present

invention that is a blend of two polyesters. These examples were tested according to the test used in the prior examples except for Gel Permeation Chromatography (GPC) which used a polystyrene standard.

5 GPC is used for determination of the molecular weight distribution averages: M_w , M_n , M_w/M_n (polydispersity), and M_z . Approximately 60 milligrams of sample is weighed and dissolved in 20 ml. of tetrahydrofuran (THF) containing toluene (internal std.) at a
10 level of 0.3% (v/v). The sample is filtered (if necessary) and then run on the GPC system. The data system generates a report showing: (1x) the molecular weight distribution averages, (2x) a time slice report, and (3x) standard, purchased from Polymer Laboratories,
15 covering a molecular weight range of 580 to 1,030,000. The mode of calibration is "Narrow MW Standard Peak Positions".

Example 1B - Preparation of Linear Water-Dispersible Polyester Composition 1

20 A 500-mL, round bottom flask equipped with a ground-glass head, an agitator shaft, nitrogen inlet, and a sidearm was charged with 73.87 g (0.445 mol) of isophthalic acid, 14.74 g (0.055 mol) of 5-sodiosulfo-
25 isophthalic acid, 81 g (0.75 mol) of diethylene glycol, 0.19 grams of titanium tetraisopropoxide and 0.847 g (0.0055 mol) of sodium acetate tetrahydrate. The flask was immersed in a Belmont bath at 200°C for two hours under a nitrogen sweep. Heating was stopped and the
30 copolyester was removed from the flask. The polymer had an inherent viscosity of 0.45 dL/g according to ASTM D3835-79 and a glass transition temperature of 29°C as measured by differential scanning calorimetry (DSC) analysis. The polymer which was transparent and
35 amorphous was extruded and pelletized. The polymer had

a weight average molecular weight (Mw) of 8,924 and a number average molecular weight (Mn) of 5,422 by GPC using a polystyrene standard.

5 Example 2B - Preparation of Branched Water-Dispersible Polyester Composition 2

 To a three-neck round-bottom flask equipped with a mechanical stirrer, a stream partial condenser a Dean-Stark trap, and a water condenser were charged the
10 following reactants: neopentyl glycol (363.38 g, 3.49 m), 5-sodiosulfoisophthalic acid (29.30 g, 0.109 m) and the catalyst, Fascat (trademark) 4100 (Atochem North America, Inc.) (0.56 g). The mixture was heated to
15 150°C and stirred under N₂ atmosphere and the temperature then gradually increased to 220°C and the distillate (water) was collected in the Dean-Stark trap until the mixture was clear (1 hr). The acid number was determined to be close to zero, and the mixture was cooled to 150°C. The second stage reactants, tri-
20 methyolpropane (75.4 g, 0.563 m), isophthalic acid (329.01 g, 1.98 m) and adipic acid (202.25 g, 1.38 m) were then added. The temperature was gradually raised to 220°C and the reaction continued for four more hours to yield a resin with an acid number of 3.6. The
25 polymer had a weight average molecular weight (Mw) of 6,241, a number average molecular weight (Mn) of 1,740 and a polydispersity index of 3.6, determined by GPC using a polystyrene standard.

30 Example 3B - Preparation of a Water-Dispersible Hot-Melt Adhesive

 A blend of the linear water-dispersible polyester polymer 1 prepared as in Example 1B (70 parts) by weight and the branched water-dispersible polyester polymer 2
35 of Example 2B (30 parts) by weight was prepared by

combining the two polymers and stirring at 225°C for 2 hours to produce the adhesive composition. The composition had a Tg of 11°C, a weight average molecular weight of 5,410, a number average molecular weight of 1,554, and a viscosity of 19,450 centipoise (19.45 Pa·s) at 350°F (175°C) as determined on a Brookfield HV: II Viscometer. The adhesive had a fast set time, as determined by a standard procedure (TAPPI Symposium, Recyclable/Repulpable Hot Melts - A Summary - U.S.A. and Europe, June, 1990, by Michael J. Ambrosini) on a corrugated kraftboard substrate, good lap shear strength (ASTM D1002 Test Method) and good tensile strength (ASTM 412 Test Method). The results are reported in Table 2. Into 100 ml of hot water (65-80°C) at a pH of 7.8, were mixed 0.5 grams of adhesive chips. Within 15 minutes under mild agitation the adhesive was completely dispersed in the water, forming a milky mixture. Repulpability results are in Tables 3 and 4.

20 Example 4B

 An adhesive composition was prepared by blending 60 parts by weight of the linear water-dispersible polymer prepared as in Example 1B with 40 parts by weight of the branched water-dispersible polyester of Example 2B and the properties of the polymer and the polymer and adhesive properties determined as in Example 3B above. The adhesive properties are reported in Table 2. The adhesive chips were dispersed in hot water as in Example 3B within 15 minutes. The adhesive had good repulping properties (see Tables 2 and 3), a Tg of 8.4°C, a weight average molecular weight of 5,272, a number average molecular weight of 1,563 and a viscosity of 17,400 centipoise (17.4 Pa·s) at 350°F (175°C).

Example 5B

An adhesive composition was prepared by blending 40 parts by weight of the linear water-dispersible polymer prepared as in Example 1B with 60 parts by weight of the
5 branched water-dispersible polyester of Example 2B and the properties of the adhesive composition determined as in Example 3B. The adhesive properties are reported in Table 2. The adhesive chips were dispersed in hot water as in Example 3B within 15 minutes. The adhesive had
10 good repulping properties (see Tables 3 and 4), a Tg of 4.2°C a weight average molecular weight of 7,622, a number average molecular weight of 1,715 and a viscosity of 2,500 centipoise (2.5 Pa·s) at 350°F (175°C).

15 Example 6B

An adhesive composition was prepared by blending 30 parts by weight of the linear water-dispersible polyester prepared as in Example 1B with 70 parts by weight of the branched water-dispersible polyester of Example
20 2B and the properties of the adhesive composition determined as in Example 3B. The adhesive properties are reported in Table 2. The adhesive chips were attempted to be dispersed in hot water as in Example 3B, however, only partial dispersion occurred. The adhesive
25 had marginal repulping properties (see Tables 3 and 4), a Tg of 4.4°C, a weight average molecular weight of 7,316, a number average molecular weight of 1,831 and a viscosity of 2,490 centipoise (2.49 Pa·s) at 350°F (175°C).

30

Table 2

PROPERTIES OF ADHESIVE COMPOSITIONS

Example No.	(a) Set Time (sec)	(b) Lap Shear (mpa)	(c) Tensile Strength (mpa)	(d) Peel Adhesion Failure Temperature °C
3B	1.7	8.6	2.9	43
4B	1.4	1.3	1.4	43
5B	1.8	4.3	.3	30
6B	3.6	4.3	.1	—

(a) TAPPI Symposium, Recyclable/Repulpable Hot Melts - A Summary, June 1990, by Michael J. Ambrosini

(b) ASTM D1002 Test Method

(c) ASTM 412 Test Method

(d) Kraft to kraft bond

Example 7B - Repulpability Test (Neutral)

Approximately 10 grams of each of the adhesives in Examples 3B, 4B, 5B, and 6B were melted, dyed, and coated onto white bond copier paper to a thickness of 1.5 to 3.0 mils (0.04 to 0.08 mm) with a wire wound rod. The coated paper was then cut to obtain a piece weighing 12 grams. The weighed coated paper was then torn into 1" by 1" (2.54 cm by 2.54 cm) pieces and placed into approximately 1000 mL of tap water in the bowl of a laboratory blender to obtain a solids to liquid consistency of ~1.2% and soaked from 1 to 4 hours. The coated paper and water were agitated at 500 rpm for 10 minutes, at 1,000 rpm for 10 minutes, and 1,500 rpm for 10 minutes. Following agitation, a portion of the slurry was removed from the bowl and diluted to produce a 0.7% solids mixture. This mixture was stirred for 30 seconds and quickly poured into a Buchner funnel that contains a 100 mesh polyester screen. A vacuum pump was attached for a short interval until the water was evacuated from the funnel and a handsheet was formed. The handsheet and screen were then removed from the funnel and excess water was blotted away with Watman 5 filter paper. The handsheet was then weighted and dried on a warm hot plate. The dried handsheet was then inspected for "stickies" using both transmitted and reflected light. The repulpability properties are reported in Table 3. This test showed that the adhesive of Example 3B is the most highly water-dispersible.

Table 3*
Repulp Evaluations Unconditional (Neutral)

EXAMPLE 3B	EXAMPLE 4B	EXAMPLE 5B	EXAMPLE 6B
Completely Dispersible	Partial	Partial	Not/Very Slightly Dispersible
Dispersion of material began immediately upon exposure of coated paper to water, producing a milky solution. Appeared to be completely dispersed after 15 minutes of soaking in water with NO AGITATION.	Material began to disperse from paper after 2 minutes in water. Material was off the paper and into milky solution after 30 minutes in water. Ring of dispersed material noticed at bottom of soaking beaker after 1 hr.	Polymer began to disperse from paper immediately on exposure to water. Nearly complete dispersion after 20 minutes soaking. Formed milky solution during soaking.	No dispersion of polymer from paper was seen during soaking period of 1 hr.
<u>HANDSHEET</u> Very little evidence of adhesive remaining in handsheet.	<u>HANDSHEET</u> Gummy residue noticed in pulping vessel following agitation. Some visible adhesive specks noticed in handsheet.	<u>HANDSHEET</u> Gummy residue noticed in pulper after agitation. Undispersed polymer and undefibered paper were noticed in handsheet.	<u>HANDSHEET</u> Gummy residue noticed in pulper after agitation. Handsheet had sticky areas of polymer throughout. Difficult to remove handsheet from filter screen after handsheet formed. Some sticky polymer remained on screen.

*Tappi, 1993, Hot Melt Symposium Procedure, Barrett

Example 8B - Repulpability in alkaline solution

5 An alkaline solution was prepared by adding 6.2 g of NaOH pellets, 3 g of tetrasodium pyrophosphate (TSPP) and 0.6 ml of Triton x-100 surfactant to 400 ml of H₂O at room temperature. The solution was warmed on a hot plate to 27°C. When the TSPP had dissolved, it was diluted to 1000 ml and adjusted to a pH of 9-12 with H₂O or base. The solution was then brought to 85°C and then 1" x 1" (2.54 x 2.54 cm) pieces of coated paper prepared as in Example 7B were added as the solution was slowly stirred at the blend station. When coated paper began to defiber, the mixer speed was adjusted to give a gentle rolling of slurry. Mixing was continued for 15-30 minutes. After defibering for 15-30 minutes, 15 slurry was diluted to 1000 ml and stirred thoroughly to assure a uniform suspension. The handsheet was formed as in Example 7B. The degree of adhesive repulpability was evaluated as in Example 7B. The results are reported in Table 4.

Table 4*
Repulp Evaluations Alkaline (pH = 10.6)

EXAMPLE 3B Completely Dispersible	EXAMPLE 4B Complete Dispersion	EXAMPLE 5B Partial	EXAMPLE 6B Partial
Dispersion began immediately upon exposure to alkaline solution. Final handsheet appeared free of dye and adhesive.	Dispersion began immediately on exposure of coated paper to alkaline solution. No adhesive apparent in handsheet.	Gummy residue noticed in pulper following agitation AND on filtration screen after formation of handsheet.	Some dispersion before agitation. Thick "pudding like" residue produced during alkaline agitation. Dried "circles" of residue were seen on filter side of handsheet. Handsheet difficult to remove from filter screen.

*Tappi, 1993, Hot Melt Symposium Procedure, Barrett

The above results show that adhesive prepared in Example 3B is best followed by Example 4B. Although the adhesive from Examples 5B and 6B were only partially repulped in alkaline solution, this is significantly improved over conventional hot melt adhesives.

Example 9B - Dispersibility of Adhesive Coated Wood Pulp

Wood pulp (5 grams) taken from a Huggies brand diaper from Kimberly Clark, was coated with 1.5 grams of the adhesive from Example 5B at 350°F (177°C). The adhesive coated wood pulp was placed in one liter of tap water (pH 7.9) at room temperature for one hour with hand stirring approximately every 10 minutes. The slurry was poured through a 600 mL Hirsch funnel pulled under vacuum at 25 psi (0.17 kPa) until water is completely removed out of the funnel. The wood pulp remained in the funnel without any sign of adhesive present in the funnel. All of the adhesive passed through the funnel into the container with the water.

Claims

1. A water-dispersible adhesive composition according to the present invention comprising a branched water-dispersible polyester composition made of the moieties of reaction products;

- (I) at least one difunctional dicarboxylic acid which is not a sulfomonomer;
- (II) 2 to 15 mol percent, based on the total of all acid, hydroxyl and amino equivalence, of residues of at least one difunctional sulfomonomer containing at least one sulfonate group bonded to an aromatic ring wherein the functional groups are hydroxyl, carboxyl, or amino;
- (III) at least one diol or a mixture of a diol and a diamine comprising:
- (A) 0.1 to 85 mol percent, based on the total mol percent of diol moieties or diol and diamine moieties, of a diol or diamine having the formula $H(-OCH_2CH_2-)_nOH$ and $HRN(-\{OH_2CH_2O\})_nNHR$ wherein n is 2 to 20 and R is hydrogen or C_1-C_6 alkyl provided that the mol percent of such moieties is inversely proportional to the value of n;
- (B) 0.1 to 15 mol percent, based on the total mol percent of diol moieties or diol and diamine moieties, of moieties of a poly(ethylene glycol) having the formula $H(-OCH_2CH_2-)_nOH$ wherein n is 2 to 500, provided that the mol percent of such moieties is

inversely proportional to the value of n ; and

- (C) 0 to greater than 99 mol percent of the diol component or diol and diamine mixture being selected from the group consisting of a glycol and a mixture of glycol and diamine having two $-NRH$ groups, the glycol containing two $-C(R^1)_2-OH$ groups wherein R^1 in the reactant is a hydrogen atom, an alkyl of 1 to 5 carbon atoms, or an aryl group of 6 to 10 carbon atoms;

- (IV) 0 to 40 mol % of a difunctional monomer reactant selected from the group consisting of hydroxycarboxylic acids having one $-C(R-)_2-OH$ group, amino-carboxylic acids having one $-NRH$ group, aminoalkanols having one $-C(R-)_2OH$ group and one $-NRH$ group and mixtures of said difunctional reactants wherein R in the reactant is hydrogen or an alkyl group of 1 to 6 carbon atoms; and

- (V) 0.1 to 40 mol % of a multifunctional reactant containing at least three functional groups selected from hydroxyl, carboxyl, amino, and mixtures thereof;

the polymer containing substantially equal mol proportions of acid equivalents (100 mol %) and diol or diol and diamine equivalents (100 mol %) wherein at least 20 weight percent of the groups linking the moieties of the monomeric units are ester linkages and wherein the inherent viscosity is at least 0.1 dL/g measured in a 60/40 parts by weight solution of phenol/tetrachloroethane at 25°C

and at a concentration of 0.25 g of polymer in 100 ml of the solvent, the glass transition temperature T_g is no greater than 20°C, and the ring and ball softening point (RBSP) is at least 70°C.

5 2. The composition according to claim 1 wherein said difunctional sulfomonomer of (II) is in a concentration of 6 to 10 mol percent.

10 3. The composition according to claim 1 wherein the moieties of (A) in the diol or mixture of diol and diamine are in a concentration of 20 to 80 mol percent and the moieties of (A) are selected from the group consisting of diethylene glycol, triethylene glycol and mixtures thereof.

15 4. The composition according to claim 1 wherein the component (A) and (B) of (III) are different moieties and the moieties of (A) are selected from the group consisting of diethylene glycol, triethylene glycol, and mixtures thereof and the moieties of (B) are in a concentration of 0.1 to 5 mol percent and are
20 selected from poly(ethylene glycols) wherein n is 5 to 50.

5. The composition according to claim 4 wherein the moieties of (B) are present at a concentration of 1 to 5 mol percent and n is 10 to 30.

25 6. The composition according to claim 1 wherein the moieties of component (C) are present in a concentration of 30 to 70 mol percent and are selected from the group consisting of neopentyl glycol, ethylene glycol, 1,3 propane diol, 1,4 butane diol, 1,6 hexane
30 diol and cyclohexane dimethanol.

7. The composition according to claim 1 wherein the moieties of (V) are present in a concentration of 0.1 to 20 mol percent.

5 8. The composition according to claim 7 wherein the moieties of (V) are present in a concentration of 2 to 6 mol percent.

9. The composition according to claim 1 wherein at least 90 weight percent of the groups linking the moieties of the monomeric units are ester linkages.

10 10. The composition according to claim 1 wherein the inherent viscosity is at least 0.2 dL/g.

11. The composition according to claim 1 wherein the number average molecular weight of the polyester composition is between 3000 and 10000.

15 12. The composition according to claim 1 wherein the T_g is between 4 and -20°C .

13. The composition according to claim 1 wherein the T_g is less than 0°C .

20 14. The composition according to claim 1 wherein the ring and ball softening point of the composition is 80 to 100°C .

25 15. The composition according to claim 1 further comprising an additional component selected from the group consisting of plasticizers, tackifiers, resins, elastomers, and low molecular weight polyolefins.

16. A water-dispersible adhesive composition comprising:

- 30 (1) 20 to 80 weight percent of the linear water-dispersible polyester composition made of the residues or moieties of reaction products;
- (i) at least one difunctional dicarboxylic acid which is not a sulfomonomer;
- (ii) 4 to 25 mol percent, based on the total of all acid, hydroxyl and amino
- 35 equivalence, of residues of at least one

- difunctional sulfomonomer containing at least one sulfonate group bonded to an aromatic ring wherein the functional groups are hydroxyl, carboxyl, or amino;
- 5 (iii) at least one diol or a mixture of a diol and a diamine comprising:
- (A) at least 15 mol percent, based on the total mol percent of diol moieties or diol and diamine
- 10 moieties, of a diol or diamine having the formula $H(-OCH_2CH_2-)_nOH$ and $HRN(OH_2CH_2O)_nNHR$ wherein n is 2 to 20 and R is hydrogen or C_1-C_6 alkyl, or
- 15 (B) 0.1 to less than 15 mol percent, based on the total mol percent of diol moieties or diol and diamine moieties, of moieties of a poly(ethylene glycol) having the
- 20 formula $H(-OCH_2CH_2-)_nOH$ wherein n is 2 to 500, provided that the mol percent of such moieties is inversely proportional to the value of n ; and,
- 25 (iv) 0 to 40 mol percent, moieties of a difunctional monomer reactant selected from hydroxycarboxylic acids, amino-
- carboxylic acids and aminoalkanols;
- the polymer containing substantially equal mol
- 30 proportions of acid equivalents (100 mol %) and diol or diol and diamine equivalents (100 mol %) wherein at least 20 weight percent of the groups linking the moieties of the monomeric units are ester linkages and wherein
- 35 the inherent viscosity is at least 0.1 dL/g

measured in a 60/40 parts by weight solution of phenol/tetrachloroethane at 25°C and at a concentration of 0.25 g of polymer in 100 ml of the solvent; and

- 5 (2) 20 to 80 weight percent of the branched water-dispersible polyester made of the moieties of reaction products;
- (a) at least one difunctional dicarboxylic acid which is not a sulfomonomer;
- 10 (b) one to 20 mol percent, based on the total of acid, hydroxyl and amino equivalents, of residues of at least one difunctional sulfomonomer containing at least one sulfonate group bonded to an aromatic
- 15 ring wherein the functional groups are hydroxyl, carboxyl, or amino;
- (c) at least one difunctional reactant selected from a glycol or a mixture of glycol and diamine having two -NRH
- 20 groups, the glycol containing two $-C(R^1)_2-OH$ groups wherein R in the reactant is hydrogen or an alkyl group of 1 to 6 carbon atoms, and R^1 in the
- reactant is a hydrogen atom, an alkyl of 1 to 5 carbon atoms, or an aryl group of
- 25 6 to 10 carbon atoms;
- (d) 0 to 40 mol % of a difunctional reactant selected from hydroxycarboxylic acids having one $-C(R-)_2-OH$ group,
- 30 aminocarboxylic acids having one -NRH group, amino-alcohols having one $-C(R-)_2-OH$ group and one -NRH group, or mixtures of said difunctional reactants wherein R in the reactant is hydrogen or

- 48 -

an alkyl group of 1 to 6 carbon atoms;
and

(e) 1 to 40 mol % of a multifunctional
reactant containing at least three
functional groups selected from hydroxyl,
carboxyl, amino, and mixtures thereof;

wherein the polyester has a predispersion pH
greater than 4 and all stated mol percents are
based on the total of all acid, hydroxyl, and amino
group containing reactants being equal to 200 mol
percent, and wherein the polymer containing a
portion of the acid-group containing reactants (100
mol percent acid) to hydroxyl and amino-group
containing reactants (100 mol %).

17. The composition according to claim 16 wherein
the concentrations of the two polyesters in the
composition are, greater than 30 but less than 80 weight
percent polyester of (1) and greater than 20 but less
than 70 weight percent of the polyester of (2).

18. The composition according to claim 17 wherein
the concentrations of the two polyesters in the
composition are, 60 to 75 weight percent of the
polyester of (1) and 25 to 40 weight percent of the
polyester of (2).

19. The composition according to claim 16 wherein
the final adhesive composition has a Tg of 4 to -20°C.

20. The composition according to claim 16 wherein
the final adhesive composition has a viscosity of 1,500
to 30,000 cP (1.5 to 30 Pa·s) at 350°F (177°C).

21. An article of manufacture comprising the hot
melt adhesive composition of claim 1 laminated between
two substrates.

22. The composition according to claim 21 wherein at least one of said substrates is selected from the group consisting of paper, paper board, and wood pulp.

23. An article of manufacture comprising the hot melt adhesive composition of claim 16 laminated between two substrates.

24. The composition according to claim 23 wherein at least one of said substrates is selected from the group consisting of paper, paper board, and wood pulp.

25. A process comprising applying in liquid form to a surface of a substrate a water-dispersible adhesive composition of Claim 16 and while remaining in the liquid form, applying a second surface of a substrate to the water dispersible adhesive composition thereby forming a laminate.

26. A process comprising applying in liquid form to a surface of a substrate a water-dispersible adhesive composition comprising a branched water-dispersible polyester composition made of the moieties of reaction products;

- (I) at least one difunctional dicarboxylic acid which is not a sulfomonomer;
- (II) 2 to 15 mol percent, based on the total of all acid, hydroxyl and amino equivalence, of residues of at least one difunctional sulfomonomer containing at least one sulfonate group bonded to an aromatic ring wherein the functional groups are hydroxyl, carboxyl, or amino;
- (III) at least one diol or a mixture of a diol and a diamine comprising:
 - (A) 0.1 to 85 mol percent, based on the total mol percent of diol moieties or diol and diamine moieties, of a diol or diamine having the formula

- 5 $H(-OCH_2CH_2-)_nOH$ and
 $HRN(\{OH_2CH_2O\})_nNHR$ wherein n is 2 to
 20 and R is hydrogen or C_1-C_6 alkyl
 provided that the mol percent of
 such moieties is inversely
 proportional to the value of n ;
 (B) 0.1 to 15 mol percent, based on the
 total mol percent of diol moieties
 or diol and diamine moieties, of
10 moieties of a poly(ethylene glycol)
 having the formula $H(-OCH_2CH_2-)_nOH$
 wherein n is 2 to 500, provided that
 the mol percent of such moieties is
 inversely proportional to the value
15 of n ; and
 (C) 0 to greater than 99 mol percent of
 the diol component or diol and
 diamine mixture being selected from
 the group consisting of a glycol and
20 a mixture of glycol and diamine
 having two $-NRH$ groups, the glycol
 containing two $-C(R^1)_2-OH$ groups
 wherein R^1 in the reactant is a
 hydrogen atom, an alkyl of 1 to 5
25 carbon atoms, or an aryl group of 6
 to 10 carbon atoms;
 (IV) 0 to 40 mol % of a difunctional monomer
 reactant selected from the group
 consisting of hydroxycarboxylic acids
30 having one $-C(R-)_2-OH$ group, amino-
 carboxylic acids having one $-NRH$ group,
 aminoalkanols having one $-C(R-)_2OH$ group
 and one $-NRH$ group and mixtures of said
 difunctional reactants wherein R in the

reactant is hydrogen or an alkyl group of 1 to 6 carbon atoms; and

(V) 0.1 to 40 mol % of a multifunctional reactant containing at least three functional groups selected from hydroxyl, carboxyl, amino, and mixtures thereof;

the polymer containing substantially equal mol proportions of acid equivalents (100 mol %) and diol or diol and diamine equivalents (100 mol %) wherein at least 20 weight percent of the groups linking the moieties of the monomeric units are ester linkages and wherein the inherent viscosity is at least 0.1 dL/g measured in a 60/40 parts by weight solution of phenol/tetrachloroethane at 25°C and at a concentration of 0.25 g of polymer in 100 ml of the solvent, the glass transition temperature T_g is no greater than 20°C, and the ring and ball softening point (RBSP) is at least 70°C, and

while remaining in the liquid form, applying a second surface of a substrate to the water dispersible adhesive composition thereby forming a laminate.

27. The process according to Claim 26 further comprising repulping said laminate in an aqueous pulping solution thereby separating said water-dispersible adhesive composition from said surfaces wherein the composition of at least one of said substrates is a fibrous material.

28. The process according to claim 26 wherein the liquid form is in the melt and the adhesive composition is a hot melt adhesive composition that is applied at a temperature of 150 to 200°C.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09J167/00 C09J177/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09J C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 052 368 (LARSON) 4 October 1977 see the whole document ---	1-14, 21-28
Y	WO,A,92 00363 (ENBOND LIMITED) 9 January 1992 see page 7, line 1 - page 8, line 25; claims 1-26 & US,A,5 098 962 (BOZICH) cited in the application ---	1-14, 21-28
Y	EP,A,0 507 244 (TOYO BOSEKI KABUSHIKI KAISHA) 7 October 1992 see claims 1-11 ---	1-14, 21-28
A	US,A,4 525 524 (TUNG ET AL.) 25 June 1985 see column 5, line 41 - line 61; claims 1,14-18 -----	1-28

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

6 April 1995

Date of mailing of the international search report

27. 04. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Decocker, L

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4052368	04-10-77	CA-A-	1096099	17-02-81
		DE-A-	2728161	29-12-77
		FR-A, B	2355892	20-01-78
		GB-A-	1579863	26-11-80
		JP-C-	1413979	10-12-87
		JP-A-	52155640	24-12-77
		JP-B-	62014594	02-04-87

WO-A-9200363	09-01-92	AU-A-	8064891	23-01-92
		US-A-	5098962	24-03-92

US-A-5098962	24-03-92	AU-A-	8064891	23-01-92
		WO-A-	9200363	09-01-92

EP-A-0507244	07-10-92	JP-A-	4304260	27-10-92
		JP-A-	6080865	22-03-94
		JP-A-	5112634	07-05-93
		US-A-	5382652	17-01-95

US-A-4525524	25-06-85	CA-A-	1248685	10-01-89
		EP-A, B	0159283	23-10-85
		JP-A-	60233127	19-11-85
		JP-A-	6184416	05-07-94
		US-A-	4585854	29-04-86
